PLASMA REFORMING/FISCHER-TROPSCH SYNTHESIS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of US. serial no. 09/560,248 filed on 4/27/2000 and issued as US Pat No.   issued on   , which was a non-provisional application claiming the benefits of provisional application No. S/N 60/131,459, filed 04/28/99.

FIELD OF THE INVENTION

This invention relates to plasma reforming of feedstocks to provide a syngas which is converted to higher molecular weight hydrocarbons using a Fischer-Tropsch (FT) reactor and process.

BACKGROUND OF THE INVENTION

Environmental, health and safety concerns are leading to requirements that offshore oil production rigs cannot flare their low value hydrocarbon gases. In such cases, the gases must be compressed for pipeline or shipboard transport to on-shore facilities. Refinery flare gases and/or bottoms can also be upgraded to more valuable products where feasible using a portion of the flare gas for feedstock and heating the reactors where necessary.

1   There have been a variety of approaches to reforming using plasmas. U.S.

2   Patent 5,993,761 to Piotr Czernichowski et al explores this area well. Charles B.

3   Benham et al explores FT synthesis as a mechanism for upgrading reformer

4   products, e.g., U.S. 5,504,118, U.S. 5,500,449; U.S. 5.620,670 and U.S. 5,621,155.

5   Both groups are working in economic niches where tax incentives, regulatory

6   penalties, etc., must combine with other factors to contribute to the worth of the use

7   of the processes. This is true even where there is a cheap raw material source, e.g.,

8   CO_2 availability from a nearby well.

SUMMARY OF THE INVENTION

10   The invention combines new plants for the manufacture of FT products

11   utilizing a plasma reformer to provide the syngas feed and the processes necessary

12   to obtain the desired FT products. The new plants include the a) reformer and FT

13   reactor combined plants in packaged form where the plants are integrated with a

14   large barge or a ship and assemblable packages, i.e., kits for plant assembly on site.

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BRIEF DESCRIPTION OF THE DRAWINGS

17   Before explaining the disclosed embodiment of the present invention in detail,

18   it is to be understood that the invention is not limited in its application to the details of

19   the particular arrangement shown, since the invention is capable of other

20   embodiments. Also, the terminology used herein is for the purpose of description

21   and not of limitation.

1   Figure 1 depicts a combined plasma reformer and Fischer-Tropsch plant for

2   the production of Fischer-Tropsch products from natural gas.

3   Figure 2 depicts a variation on the reactor of Fig. 1 adapted for the production

4   of Fischer-Tropsch liquids from liquids such as H-Oil and solids such

5   as petroleum coke slurries.

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DETAILED DESCRIPTION OF THE DRAWINGS

The process of Figure 1 is carried out in a plasma reforming reactor 9. The

10   electrical feed 10 is conditioned by power supply 11 to operate within the frequency

11   range of 0.37=0.44 mHz. The conditional feed 10 is supplied to plasma generator

12   12 which initiates and controls the plasma formation in the reactor 9. A methane gas

13   or other low molecular weight gaseous hydrocarbon feed 13 is heated to about

14   400°C for purposes of this discussion and introduced into reactor 9 directly or

15   through the plasma generator 12. Steam 14 is also fed to reactor 9. Carbon dioxide

16   can also be introduced into reactor 9 as a substitute for steam to reduce to eliminate

17   any carbon deposition on the catalyst.

18   Preconditioned "tap" or other water is stored in boiler feed water tank 15

19   before injection into boiler 16 where it is preheated by heat exchange with the hot

20   gases from reactor 9 and introduced into reactor 9. The 900°-1000°C gases from

21   reactor 9 are cooled in boiler 16 and introduced into gas feed preheater 17 where it

22   is used to heat the gas feed. The cooled reactor 9 effluent is then run through

1   compressor 18 and introduced into a FT reactor 19 at about 250°C and 225 psia.

2   Reactor 19 temperatures are regulated, inter alia, by heat exchange coil 21.

3   The reaction products from FT unit 19 are cooled in condenser 24 with 60°C

4   plant water. The cooled reaction products are then separated into gaseous and

5   liquid fractions in separator 25. The gases are condensed in condenser 24 with

6   about 10°C coolant and passed through gas/liquid separator 25 to break out a

7   water/oil fraction. The gases are passed through the hydrogen separator 26. The

8   tail gas is recycled to the preheater 17 and fed to the reactor 9. The product

9   fractions from the FT reactor 9 further include wax/oil, water/oil and hydrogen.

10   Computer runs were made to evaluate the operation of the plant of Fig. 1. In

11   the case of natural gas, both tail gas recycle after hydrogen removal and carbon

12   dioxide recycle were investigated. In the other two cases, tail gas recycle without

13   hydrogen removal and carbon dioxide recycle were investigated. In all cases, the

14   feedstock flow-rate was 1000 tons per day.

15   The outlet pressure of the plasma reactor was assumed to be 15 psia and the

16   outlet temperature was 1832°F for natural gas and 2100°F for the other two

17   feedstocks. It was assumed that the gases at the outlet of the plasma reactor were

18   in equilibrium at the exit temperature. The efficiency of the plasma in converting

19   electrical energy into thermal energy was assumed to be 70%. The FT reactor inlet

20   pressure was assumed to be 250 psia. Therefore, compression of the synthesis gas

21   exiting the plasma rector was required. The compression power was calculated

1   using an isentropic efficiency of 70%. It was assumed in all cases that the FT

2   reactor converted 90% of the incoming carbon monoxide. The liquid hydrocarbon

3   products (C_5+) produced in the FT reactor were modeled assuming a dual-slope

4   Anderson-Schultz-Flory carbon number distribution (αl = 0.69 and $\alpha 2$ = 0.95). a

5   water gas shift constant of 10 was assumed. It was assumed that electrical power

6   would be produced by a combined cycle unit from the tail gas (which was not

7   recycled) at an efficiency of 55% based on lower heating value. It was further

8   assumed that additional electric power would be generated from steam derived from

9   cooling the plasma and FT outlet gases and from cooling the FT reactor. The

10 efficiency of the steam-generated power was assumed to be 33%.

11 The following composition of natural gas was used in the calculations:

12 CH_4 89.00 vol % tail gas

13 C_2H_6 6.63

14 C_3H_8 0.71

15 CO_2 2.95

16 N_2 0.71

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18 A diagram of a plasma-based system for reforming natural gas is shown in

19 Fig. 1. In Table 1, results are tabulated for a natural gas feedstock with recycle of

20 tail gas from the FT reactor and removal of hydrogen from the system. The first

21 entry having 0% tail gas recycle is a baseline case wherein 30% of the hydrogen

22 from the plasma reactor is removed upstream of the FT reactor to reduce the H_2:CO

23 ratio of the gas exiting the plasma reactor from 2.85 to 1.99 which is considered to

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1   be a practical maximum value for an iron-based FT catalyst. In the other cases in

2   Table 1, 90% of the hydrogen is removed downstream of the FT reactor (from the

3   tail gas). With the requisite amount of steam added to the plasma reactor, the

4   minimum possible H_2:CO ratio is 1.55 when 90% tail gas recycle is employed. It can

5   be seen that increased steam addition increases the H_2:CO ratio and decreases

6   hydrocarbon yield.

TABLE 1. Plasma Reforming of Natural Gas with Tail Gas Recycle

. Tail Gas Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.064	1.99	3.118	7.317	3.986
90	1.281	1.55	5.413	5.403	4.152
90	1.486	1.6	5.401	5.486	4.203
90	1.894	1.7	5.384	5.644	4.302
90	2.298	1.8	5.372	5.798	4.400
90	2.697	1.9	5.360	5.947	4.495

In Table 2 are shown the results for the case wherein CO_2 is removed from

10   the tail gas and recycled to the plasma reactor. In this case no H_2 removal is

11   necessary since the hydrogen reacts with the CO_2 in the plasma reactor. The

12   minimum amount of steam required in this case is about 0.65 pounds per pound of

13   natural gas fed to the plasma reactor. This gives a H_2:CO ratio of 1.6. As additional

14   steam is added to increase the H_2:CO ratio to 1.9, the yield increases slightly but the

15   energy required by the plasma increases significantly. The tail gas recycle case

16   which produces the highest C_5+ yield produces about 21% more yield than the best

1   CO_2 recycle case, but this tail gas recycle case requires about 11% more electrical

2   energy to be imported.

3   **TABLE 2. Plasma Reforming of Natural Gas with CO_2 Recycle**

CO_2 Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.064	1.99	3.118	7.317	3.986
98	0.647	1.60	4.413	5.623	3.322
98	1.073	1.70	4.443	5.797	3.476
98	1.492	1.80	4.461	5.964	3.621
98	1.851	1.90	4.467	6.132	3.740

A diagram of a system for reforming refinery bottoms (H-Oil) is shown in Fig. 2.

In the plant of Figure 2, the tail gas recycle loop and the hydrogen separator are eliminated. A condenser is added with the elimination of hydrogen as a product and the addition of alcohols. The same identification numerals used in Fig. 1 are utilized in Fig. 2 except as new elements are added. Modifications are indicated by the addition of alphabetic suffixes.

The H-Oil feed 13a is pumped into reactor 9 along with steam from source 14. The reactor 9 products are piped to boiler 16 from whence steam is recycled to reactor 9 via source 14. The reactor 9 products are used to heat the recycled tail gas via the preheater 17a prior to its return to the inductively coupled plasma generator 12 and reactor 9. Where the H-oil is sour, it is desulfurized in separator

20, passed through compressor 18a and introduced into FT reactor 19. Boiler feed water 15 is passed through coil 21 to form 450 psig steam for recycle to reactor 9.

The FT products from FT reactor 19 are passed through boiler 27 to heat boiler feed water for recycle. The cooler FT products are then passed through condenser 22 for further cooling and then through separator 25a to separate oil, water and alcohols from the tail gas to be recycled for use as fuel and feed for reactor 9.

The composition of H-Oil used in the calculations is as follows:

	Wt.%
Carbon	84.33
Hydrogen	8.89
Nitrogen	1.12
Sulphur	5.56
Ash	0.10

The higher heating value of the H-Oil is 17,084 Btu per pound. As in the natural gas case, calculations were performed for a) recycle of a portion of the tail gas to the plasma reactor and b) for separation of carbon dioxide from the tail gas and recycling a portion of the carbon dioxide to the plasma reactor. Due to the lower hydrogen content of H-Oil compared to natural gas, hydrogen removal from the system is not required. In Table 3, calculated results are tabulated for different amounts of recycle of tail gas. As tail gas recycle is increased, the amount of steam required is reduced and the hydrocarbon yield is increased by 67%. Also, the

1   plasma energy requirement drops by 21% as tail gas recycle increases. However,

2   the amount of electrical energy imported increases by 44% as the tail gas recycle

3   increases.

4   **TABLE 3. Plasma Reforming of H-Oil with Tail Gas Recycle**

Tail Gas Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.379	1.65	3.509	6.020	2.871
10	1.354	1.63	3.683	5.892	3.055
20	1.317	1.60	3,881	5.755	3.216
30	1.268	1.56	4.099	5.613	3.381
40	1.215	1.51	4.342	5.471	3.542
50	1.151	1.44	4.615	5.325	3.698
60	1.086	1.35	4.919	5.184	4.127
70	0.954	1.19	5.270	5.013	3.974
80	0.762	0.92	5.661	4.838	4.074
85	0.643	0.70	5.864	4.780	4.133

      In Table 4 are shown the results for the H-Oil feedstock wherein CO_2 is

7   removed from the tail gas and recycled to the plasma reactor. As CO_2 recycle is

8   increased, the amount of steam required is reduce and the H_2:CO ratio decreases.

9   The yield increases by 27% and the amount of imported electrical energy increases

10   by about 19%. The 85% tail gas recycle case which produces the highest C_5+ yield

11   produces about 31% more yield than the best CO_2 recycle case, but the tail gas

12   recycle case requires about 21% more electrical energy to be imported.

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1   **TABLE 4. Plasma Reforming of H-Oil with CO_2 Recycle**

CO_2 Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.379	1.65	3.509	6.020	2.871
10	1.353	1.57	3.580	5.953	2.922
20	1.304	1.47	3.661	5.868	2.971
30	1.235	1.37	3.753	5.768	3.019
40	1.188	1.27	3.851	5.689	3.085
50	1.092	1.15	3.970	5.575	3.142
60	1.024	1.03	4.100	5.490	3.227
70	0.903	0.90	4.260	5.373	3.310
80	0.741	0.75	4.457	5.240	3.404

2   Figure 2 provides for a solid feedstock. Petroleum coke is utilized here. The

3 only difference between this process and the H-Oil process is that water must be

4 used rather than steam to form the solid petroleum coke slurry. The latent heat of

5 vaporization of the water must be supplied by the plasma; therefore, reforming of

6 solids is less energy efficient than reforming liquids or gases. The assumed

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8 composition of petroleum coke used in the calculations is:

9   **Wt%**

10   Carbon   88.94

11   Hydrogen   3.92

12   Oxygen   0.10

13   Nitrogen   1.51

14   Sulphur   5.53

15   Ash   0.50

1   The higher heating value of the petroleum coke is 15400 Btu per pound. As

2   in the previous case, calculations were performed for a) recycle of a portion of the

3   tail gas to the plasma reactor and b) for separation of carbon dioxide from the tail

4   gas and recycling a portion of the carbon dioxide to the plasma reactor. Due to the

5   low hydrogen content of petroleum coke, hydrogen removal from the system is not

6   required. In Table 5, calculated results are tabulated for different amounts of recycle

7   of tail gas. As tail gas recycle is increased, the amount of steam required is reduced

8   and the hydrocarbon yield is increased by 39%. Also, the plasma energy

9   requirement drops 21% as tail gas recycle increases. Unlike the H-Oil case, the

10   amount of electrical energy imported decreases as tail gas recycle increases.

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12   **TABLE 5. Plasma Reforming of Petroleum Coke with Tail Gas Recycle**

Tail Gas Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.468	1.30	3.469	7.082	5.058
10	1.420	1.25	3.643	6.836	4.465
20	1.374	1.20	3.833	6.605	4.507
30	1.334	1.14	4.040	6.385	4.555
40	1.261	1.06	4.272	6.124	4.565
50	1.165	0.95	4.531	5.850	4.558
60	1.046	0.80	4.815	5.575	4.537

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14   Figure 2 provides for the introduction of a petroleum coke or other slurry, e.g.,

15   a coal slurry, through slurry pump 13b.

1   In Table 6 are shown the results for the petroleum coke feedstock wherein

2   CO_2 is removed from the tail gas and recycled to the plasma reactor. As CO_2

3   recycle is increased, the amount of steam required is reduced and the H_2:CO ratio

4   decreases. The yield increases by 18% and the amount of imported electrical

5   energy decreases by about 17%. The 60% tail gas recycle case which produces the

6   highest C_5+ yield produces about 17% more yield than the best CO_2 recycle case,

7   but the tail gas recycle case requires about 8% more electrical energy to be

8   imported.

TABLE 6. Plasma Reforming of Petroleum Coke with CO_2 Recycle

CO_2 Recycle %	Steam Fed to Plasma Lb/Lb Feed	FT H_2:CO	Yield C_5+ Bbl/ton Feed	Plasma Energy kWh/Lb C_5+	Imported Energy kWh/Lb C_5+
0	1.468	1.30	3.469	7.082	5.058
10	1.415	1.21	3.547	6.917	4.391
20	1.371	1.12	3.629	6.775	4.373
30	1.292	1.02	3.727	6.568	4.312
40	1.216	0.92	3.835	6.379	4.271
50	1.132	0.82	3.958	6.184	4.235
60	1.022	0.70	4.103	5.959	4.186

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11   Based on the calculations, the following conclusions can be drawn:

12   i)   Tail gas recycle is generally superior to carbon dioxide recycle.

13   ii)   Carbon dioxide removal prior to the FT reactor is unnecessary at the

14   low plasma pressure assumed.

15   iii) In all cases, imported electrical power will be required.

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GENERAL TEACHING OF THE INVENTION

Preferably, a natural gas feed is utilized as a raw material but refinery residuals such as H-oil, and coal or coke can also be utilized as feeds in variations of the overall process just described. The plant can be a prefabricated unit mounted on a barge or larger vessel, a unit assembled on an oil or gas offshore platform, or other site, or a "kit" made up of the components of a predesigned plant packaged for usage under the conditions required to effectively recover FT products. The feedstocks are preferably hydrocarbons but can include oxygen, nitrogen, sulphur and various other elements to the extent that the substantially hydrocarbon characteristics of the feedstock remain present. Thus, where sulphur, various metals, or other materials are a component of the feedstock, the plant must include equipment and ancillary process steps necessary for removing these materials. Similarly, solid feedstocks must be ground to predetermined sizes for assembly at a coal field or other deposit. Where the feedstock is solid, e.g., coal or a coke, it must be ground to a powder of predetermined sized particles.

Although the present invention has been described with reference to preferred embodiments, numerous modifications and variations can be made within the scope of the invention. No limitation with respect to the specific embodiments disclosed herein is intended or should be inferred.